

METHOD FOR COPOLYMERIZATION AND  
RESULTING COPOLYMERS

125B<sub>1</sub>

The present invention relates to a novel method  
5 of preparing block copolymers, and to certain of these  
block copolymers.

Block copolymers are widely known. However, it  
is also known that it is difficult to prepare block  
copolymers one of whose blocks is a polyolefin (PO),  
10 especially if the desire is that the alpha-olefin  
should be inserted in a regular manner in order to give  
a stereoregular and/or regioregular copolymer. It is  
also known that it is (virtually) impossible to prepare  
block copolymers whose two blocks are polyolefins,  
15 whether crystalline or amorphous.

Yamahiro et al., Macromol. Chem. Phys. 200,  
134-141 (1999), describes a process of stopped-flow  
polymerization for obtaining "true" PP/EP block  
copolymers. However, the copolymers produced are  
20 limited in terms of molecular mass, since they have a  
molecular weight  $M_n$  of less than or equal to 16 000 and  
a polydispersity index of between 3.0 and 3.3. Other  
molecular mass characteristics are excluded by this  
type of technique: in particular, higher molecular  
25 masses cannot be attained, since they are a function of  
the polymerization time, which can only be short (of  
the order of from 0.1 to 0.2 s) and in any case less  
than the growth time of a chain; in particular, also,  
lower polydispersity indexes cannot be attained, since  
30 stopped-flow polymerization is not a true poly-  
merization with living species, but comprises a large  
number of transfer reactions.

Therefore, there is to date no true PP/EP  
copolymer, with a PP block and an EP block linked  
35 together, which has a sufficient molecular mass. This  
PP/EP copolymer is a crystalline PO/amorphous PO  
copolymer, which would find advantageous application in

PP/EP polymer blends. In these blends, the crystalline PP forms the continuous phase, which is modified by the addition of EP copolymer (more specifically EPR, which is elastomeric) which forms a nodular disperse phase. A true copolymer added to this blend would play a part similar to that played by an emulsifier in emulsions, improving the compatibility of the phases, and ultimately would enhance the impact/rigidity trade-off.

This same problem of difficulty in preparing "true" block copolymers occurs with copolymers one of whose blocks is a block of a polar monomer, such as MMA.

The patent application EP-A-0634429 in the name of Mitsui describes the preparation of block copolymers, one block being a polyolefin and one block being derived from a vinyl, vinylidene or lactone monomer. The catalyst used is an alkyl complex of a metal from the rare earth group, with bridged cyclopentadiene rings (bridged by a dimethylsilylene group). This document describes in particular the catalyst  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuCp})_2\text{YCH}(\text{SiMe}_3)_2$ , with - optionally - a THF-type donor complexed to the metal. The copolymers obtained, however, are not satisfactory, since the polyolefin fraction represents too low a fraction of the final copolymer. Moreover, if the polydispersity values appear to be acceptable, it is only because these values are derived from the PMMA fraction, representing the quasitotality of the copolymer. Moreover, the catalysts do not in fact provide true copolymers. In effect, extensive transfer reactions (that is, the reactions which put an end to the living nature of the polymerization) lead to the formation not of true copolymers but of a mixture of homopolymers and copolymers. Moreover, the reaction times are fairly long.

The article by Yasuda et al., Tetrahedron, Vol. 51, No. 15, pp. 4563-4570, 1995, describes hydride derivatives of lanthanides in the form of a complex

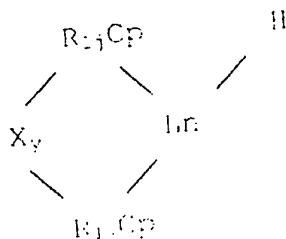
with bridged cyclopentadiene rings (bridged by a dimethylsilylene group), these cyclopentadiene rings carrying substituents which have a significant steric bulk ("bulky substituent"). This document describes in particular the hydride catalyst  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2\text{tBuSiCp})_3\text{YH}$  (represented in its dimer form). These compounds are obtained in situ by hydrogenolysis of the starting alkyl derivative, and are then used for the polymerization of alpha-olefins. Although such compounds are described as having an alpha-olefin polymerization activity greater than that of the alkyl derivatives from which they are derived, the polymerization times are still very long, of the order of half a day or a day.

These hydride catalysts also have the classic disadvantage of hydrides, namely that hydride derivatives are known to be unstable and to break down rapidly at high temperature.

The search is therefore on for an effective method of preparing block copolymers: particularly, on the one hand, copolymers one of whose blocks includes a polar fraction, and, on the other hand, copolymers whose two blocks are polyolefins.

The invention accordingly provides a method of preparing block copolymers, comprising the steps of polymerizing a first monomer using an organolanthanide catalyst in which said catalyst is in the form of a hydride complex of a trivalent metal from the rare earth group, then polymerizing at least one second monomer.

In one embodiment, the hydride complex of a trivalent metal from the rare earth group has the formula I:



in which:

Cp is a cyclopentadienyl radical;  
 R<sub>1</sub>, identical or different at each occurrence,  
 is a substituent of the cyclopentadienyl group  
 and is an alkyl radical or a silicon-containing  
 hydrocarbon radical, containing from 1 to  
 20 carbon atoms, and with the Cp ring to which  
 it is linked optionally forming an indenyl or  
 fluorenyl ring system, it being possible  
 optionally for each R<sub>1</sub> to be substituted;  
 j, identical or different at each occurrence,  
 is an integer from 1 to 5 inclusive;  
 X is a divalent alkylene radical or a divalent,  
 silicon-containing hydrocarbon radical, con-  
 taining from 1 to 20 carbon atoms, optionally  
 containing other heteroatoms such as oxygen;  
 y is 1 or 2;

Ln is a trivalent metal from the rare earth  
 group, selected from Y, Sc, La, Ce, Pr, Nd, Pm, Sm, Eu,  
 Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

In one embodiment, in the formula I, X is  
 Si(R)<sub>2</sub> in which R is an alkyl radical having from 1 to  
 4 carbon atoms.

In one embodiment, in the formula I, R<sub>1</sub> is an  
 alkyl radical or a silicon-containing hydrocarbon  
 radical, containing from 1 to 6 carbon atoms, which is  
 unsubstituted, and j is 1, 2 or 3.

In one embodiment, in the formula I, R<sub>1j</sub>Cp is  
 the group 2-Me<sub>3</sub>Si, 4-Me<sub>2</sub>tBuSiCp or the group  
 2-Me<sub>3</sub>Si, 4-tBuCp.

In one embodiment, in the formula I, Ln is Y or

Sm. In one embodiment, the catalyst is

$\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2\text{tBuSiCp})_2\text{YH}$  or

$\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuCp})_2\text{SmH}$ .

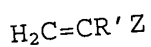
5 In one embodiment, the catalyst is racemic.

In one embodiment, the catalyst is generated in situ in the presence of at least one portion of the first monomer.

10 In one embodiment, the blocks are homopolymers or random copolymers.

In one embodiment, the block copolymer comprises a block of the first monomer which is an alpha-olefin and a block of the second monomer which is a vinyl, vinylidene or lactone compound.

15 In this embodiment, the vinyl or vinylidene compound is represented by the formula



20 in which  $\text{R}'$  is hydrogen or an alkyl radical having from 1 to 12 carbon atoms and  $\text{Z}$  is an electron-withdrawing radical.

In this embodiment, the vinyl or vinylidene compound is an ester of an unsaturated carboxylic acid.

In this embodiment, the polyolefin is crystalline.

25 In one embodiment, the second monomer is polar.

In one embodiment, the method is for preparing a PO/PMMA or PO/PL copolymer.

In this embodiment, the PO block is an iPO block.

30 In one embodiment, the block copolymer comprises a block of the first monomer which is a first alpha-olefin and a block of the second monomer which is a second alpha-olefin.

35 In a variant of this embodiment, the first polyolefin is crystalline and the second polyolefin is crystalline.

In this variant, the copolymer is a PP/PE copolymer.

In another variant of this embodiment, the first polyolefin is crystalline and the second polyolefin is amorphous.

In this variant, the copolymer is a PP/EP  
5 copolymer.

In one embodiment, the PP block is an iPP block.

The invention also provides a copolymer comprising a first block of a crystalline polyolefin  
10 and a second block of an amorphous polyolefin, with the exception of a PP/EP copolymer having a molecular mass  $M_n$  of less than or equal to 16 000 and a polydispersity index of between 3 and 3.3.

In one embodiment, the copolymer is a PP/EP  
15 copolymer, particularly one in which the PP block is an iPP block.

The invention also provides a copolymer comprising a first block of a crystalline polyolefin and a second block of a crystalline polyolefin.

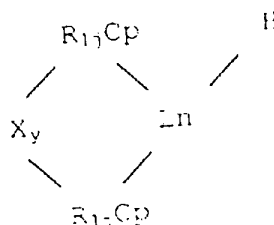
The invention also provides a copolymer  
20 comprising a first block of an amorphous polyolefin and a second block of an amorphous polyolefin.

In one embodiment, the blocks are homopolymers or random copolymers.

The invention is now described in greater  
25 detail in the following description.

#### Catalyst.

The catalyst is an organolanthanide in the form  
of a hydride complex of a trivalent metal from the rare  
30 earth group (bridged); advantageously it has the formula I:



in which:

Cp is a cyclopentadienyl radical, substituted preferably in positions 2 and 4;  
 $R_1$ , identical or different at each occurrence, is a substituent of the cyclopentadienyl group and is an alkyl radical or a silicon-containing hydrocarbon radical, containing from 1 to 20 carbon atoms, in particular from 1 to 6 carbon atoms, optionally forming an indenyl or fluorenyl ring system with the Cp ring to which is linked, it being possible optionally for each  $R_1$  to be substituted, for example, by up to 3 halogens;

$j$ , identical or different at each occurrence, is an integer from 1 to 5 inclusive, in particular  $j$  is 1, 2 or 3;

in particular  $R_{1j}Cp$  is the group 2-Me<sub>3</sub>Si,4-Me<sub>2</sub>tBuSiCp, or the group 2-Me<sub>3</sub>Si,4-tBuCp;

X is a divalent alkylene radical or a divalent, silicon-containing hydrocarbon radical, containing from 1 to 20 carbon atoms, optionally containing other heteroatoms such as oxygen, in particular of formula Si(R)<sub>2</sub> where R is an alkyl radical having 1 to 4 carbon atoms, in particular SiMe<sub>2</sub>;

y is 1 or 2, preferably 1;

Ln is a trivalent metal from the rare earth group, selected from Y, Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, in particular Y and Sm.

Examples of catalysts are  
 $Me_2Si(2-Me_3Si,4-Me_2tBuSiCp)_2YH$  and  
 $Me_2Si(2-Me_3Si,4-tBuCp)_2SmH$ .

The catalyst may in fact have ligands which are similar to those found for the catalysts known as "group IV" or metallocene or Kaminsky catalysts. A restricted geometry may also be envisaged, and also ligands other than those described above in relation

with the formula I.

In one variant, the catalyst is in a racemic form. This form makes it possible to obtain isotactic polymers.

5       The catalysts of the invention in hydride form are prepared, for example, by hydrogenation from the alkyl precursor, for example by application of molecular hydrogen. The alkyl precursors are described, for example, in the document EP-A-0634429 in the name  
10 of Mitsui. This operation may be performed by dissolving the alkyl starting product in a solvent (aliphatic or aromatic hydrocarbon) or suspending it in a nonsolvating hydrocarbon (aliphatic or aromatic hydrocarbon), followed by contact with molecular  
15 hydrogen.

#### Polymerization method

The polymerization is very effective in particular with the catalyst formed in situ in the presence of the monomer. The proof of this efficacy is  
20 the exothermicity of the reaction mixture when the hydrogen is introduced, thereby demonstrating that the polymerization reaction is initiated immediately. Accordingly, each alkyl precursor leads to a potentially polymerizing hydride species, which leads  
25 effectively to a polymerization. In the case of the preparation of copolymers, this formation in situ in the presence of the monomer is not necessary; it is, however, preferred.

The method may be implemented with or without  
30 solvent. In the case without solvent, it is the liquid monomer itself which plays this part. In the case with solvent, the monomer (in solution or in suspension) may be in gaseous, liquid or solid form.

The polymerization medium may therefore be a  
35 solvent, mass or gaseous medium.

The solvent, when used, may be an aliphatic or aromatic hydrocarbon, such as toluene.

The reaction temperature is generally between



-78°C and 150°C, preferably from 0 to 100°C.

The reaction pressure is generally between standard pressure and 200 bar, preferably between 1 and 20 bar.

5       The reaction time is generally between a few seconds and a few hours.

The monomer (or monomer mixture) may be added in one go or gradually, in a controlled way.

10       The above conditions apply to the polymerization steps in the case both of homopolymers and copolymers, and even of terpolymers (or more if necessary).

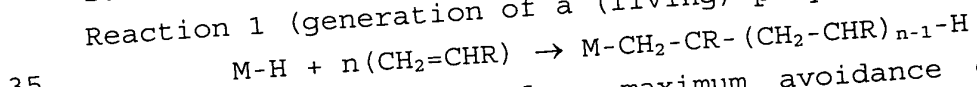
15       In the case where copolymers are prepared, the second monomer is added, for example, directly to the reaction mixture from the first step. If a solvent has been used during this step, it may either be retained or removed by customary techniques, taking care not to degrade the living species carrying the polyolefinic chain from the first step, and optionally replaced by  
20       another solvent.

The present polymerization method is efficient in that:

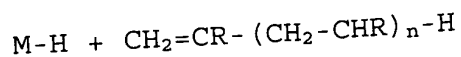
- 25       - it makes it possible to generate poly-alpha-olefins of controlled mass, by limiting the transfer reactions
- the poly-alpha-olefin species is living and in a second step is able to polymerize another monomer (olefinic, vinylic, etc.), in order to lead to the corresponding block  
30       copolymer.

30       The reaction scheme is as follows (where M-H signifies the organolanthanide catalyst in hydride form).

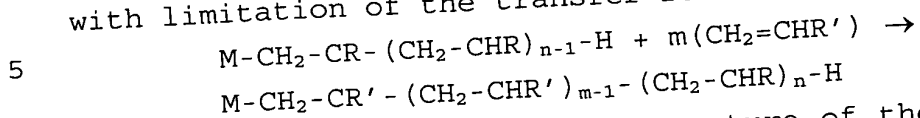
Reaction 1 (generation of a (living) polyolefin)



There is therefore maximum avoidance of the transfer reaction which produces the following final polymer species:



Reaction 2 (addition to the living, growing polyolefin of the second monomer, to give the block copolymer, with limitation of the transfer reaction)



Advantageously, the temperature of the reaction mixture will be controlled. In order to do this, it will be possible to supply the reactor continuously with the monomer; this will make it possible in particular to limit the initial exothermicity.

10 In the case where it is desired to obtain copolymers, the first step will be implemented under conditions similar to those for the homopolymers, and then the second monomer will be added to the reaction mixture still containing a living species.

The (co)polymers thus obtained are separated by conventional techniques.

Polymers prepared in the invention.

20 The polymers prepared as claimed in the invention may be homopolymers or random copolymers (the two or more monomers being present simultaneously in the reaction mixture) or may be blocked copolymers, or even terpolymers or more if necessary.

25 The homopolymer, or one copolymer block, may be isotactic, particularly when the catalyst is in a racemic form (and when the monomer is prochiral).

30 Examples of homopolymers are poly-alpha-olefins, the olefin containing for example from 3 to 20 carbon atoms. Examples of olefins are propylene, 1-butene, 1-hexene, 1-heptene, 1-octene, 1-decene, etc.

Examples of random copolymers are the copolymers of the above olefins, or copolymers based on ethylene.

35 Examples of block copolymers are copolymers containing a block of the first monomer, which is an alpha-olefin, and a block of the second monomer, which is a vinyl, vinylidene or lactone compound.

Examples of vinyl or vinylidene compounds are represented by the formula  $H_2C=CR'Z$ , in which  $R'$  is hydrogen or an alkyl radical having from 1 to 12 carbon atoms and  $Z$  is an electron-withdrawing radical.

5        Examples of such groups are the esters of an unsaturated carboxylic acid, especially (meth)acrylic acid. Mention may be made of methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, phenyl acrylate, methyl methacrylate, ethyl methacrylate, 10    propyl methacrylate, n-butyl methacrylate and phenyl methacrylate.

      Examples of lactones include the cyclic esters possessing from 3 to 10 carbon atoms, and are preferably propyllactone, valerolactone and capro- 15    lactone.

      The polyolefin (PO) block may be crystalline, whereas the block of the second monomer may be polar.

      Specific examples of such copolymers are the copolymer PO/PMMA, especially iPO/PMMA, and PO/PL 20    (polylactone) copolymer, especially iPO/PL.

      Examples of block copolymers are copolymers containing a block of the first monomer, which is a first alpha-olefin, and a block of the second monomer, which is a second alpha-olefin.

25        Such examples of copolymers include in particular those in which the first polyolefin is crystalline and the second polyolefin is crystalline, especially a PP/PE copolymer.

      Such examples of copolymers include in 30    particular those in which the first polyolefin is crystalline and the second polyolefin is amorphous, especially a PP/EP copolymer.

      The above PP block is, for example, an iPP block.

35        The invention also provides copolymers which are "true" block copolymers, in contradistinction to the copolymers of the prior art, which provides copolymers which are mixtures.

The molecular weight of the homopolymers or copolymers may vary within a wide range, between 500 and  $10^8$ , preferably between 5 000 and  $10^6$ . The ratio, in one copolymer, between the monomers A and B may also vary within a very wide range, from 99/1 to 1/99.

The invention therefore also provides copolymers as described above.

In particular, the invention provides block copolymers of the PP/EP (crystalline PO/amorphous PO) type, with the exception of those described in the publication Yamahiro et al., Macromol. Chem. Phys. 200, 134-141 (1999), namely in particular those whose molecular weight  $M_n$  is less than or equal to 16 000 and whose polydispersity index is between 3.0 and 3.3. The invention therefore provides in particular block copolymers of the PP/EP type with a molecular weight greater than 16 000, in particular greater than 20 000, especially greater than 50 000, and copolymers of the PP/EP type whose polydispersity index is less than 3, in particular less than 2.5, especially less than 2.

The examples which follow illustrate the invention without limiting it.

Preparation of complex 1:  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_2)_2\text{Sm}(\text{THF})_2$

A solution of  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_3)_2$  (3.01 g, 6.77 mmol) in 60 ml of THF is admixed with 8.2 ml of a 1.66M solution of nBuLi in hexane, i.e., 13.5 mmol, at 0°C. Following reaction of the mixture at ambient temperature for 6 h with stirring, 20 ml of a 0.68M solution of tBuOK in THF, 13.6 mmol, are added. The mixture is refluxed for 12 h and the solution is evaporated to dryness. The product is washed with twice 30 ml of hexane, leading to the potassium disalt of  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_3)_2$  in the form of white powder (yield = 70%). A suspension of 5.64 g (10.8 mmol) of the potassium disalt of  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_3)_2$  in 80 ml of THF and 10 mmol of  $\text{SmI}_2$  in 80 ml of THF are added at the same time to 40 ml of THF at -80°C. The

reaction mixture is then refluxed for 12 h and the solution is subsequently evaporated to dryness. 50 ml of toluene are added to the residue and the solid obtained is separated by centrifuging. Following removal of the solvent under vacuum, the residue is extracted with twice 15 ml of THF. Recrystallization from a THF/hexane mixture leads to 1 in the form of a violet solid (yield = 35%).

Preparation of complex B:  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2, \text{tBuSiC}_5\text{H}_2)_2\text{YCH}(\text{SiMe}_3)_2$

A solution of  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2, \text{tBuSiC}_5\text{H}_2)_2\text{YCl}_2\text{Li}(\text{THF})_2$  (2 g, 2.3 mmol) in 60 ml of toluene is admixed with 4.5 ml of a 0.79M solution of  $(\text{Me}_3\text{Si})_2\text{CHLi}$  in  $\text{Et}_2\text{O}$ , i.e., 3.5 mmol, at  $0^\circ\text{C}$ . The mixture is stirred from  $0^\circ\text{C}$  to ambient temperature for 13 hours, after which the solvent is evaporated under vacuum. 80 ml of hexane are added to the residue and the suspension is stirred for 24 hours. The insoluble solid is recovered by centrifuging and is recrystallized from hexane to give B - yield = 36%.

Preparation of complex C:  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuSiC}_5\text{H}_2)_2\text{SmCH}(\text{SiMe}_3)_2$

A solution of  $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuSiC}_5\text{H}_2)_2\text{SmCl}_2\text{Li}(\text{THF})_2$  (2.3 mmol) in 60 ml of toluene is admixed with 4.5 ml of a 0.79M solution of  $(\text{Me}_3\text{Si})_2\text{CHLi}$  in  $\text{Et}_2\text{O}$ , i.e., 3.5 mmol, at  $0^\circ\text{C}$ . The mixture is stirred from  $0^\circ\text{C}$  to ambient temperature for 13 hours, after which the solvent is evaporated under vacuum. 80 ml of hexane are added to the residue and the suspension is stirred for 24 hours. The insoluble solid is recovered by centrifuging and is recrystallized from hexane to give C - yield = 28%.

#### Example 1:

20 ml of distilled toluene are introduced, using a syringe, into a Schlenk tube (dried at  $100^\circ\text{C}$  for 2 h beforehand), connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. The toluene is degassed

and then saturated with argon. Catalyst 1 (7.4 mg -  
0.01 mmol) is introduced and stirring is maintained  
until it has completely dissolved. Then 2 ml of  
1-pentene are introduced through the septum using a  
5 syringe. Polymerization is continued for 12 hours at  
ambient temperature with stirring. To neutralize the  
catalyst at the end of the reaction, 10 ml of methanol  
are injected. The precipitated polymer is then isolated  
by centrifuging, washed with twice 10 ml of methanol  
10 and dried under vacuum for 3 hours. The catalytic  
activity is 161 g of polymer/mol of catalyst/h. The  
polymer possesses the following characteristics:  
Mn = 10 600. The chain incorporation of the monomer is  
isotactic (mm > 95%).

15 Example 2:

The procedure of example 1 is repeated except  
that the 1-pentene is replaced by 2 ml of 1-hexene. The  
catalytic activity is 138 g of polymer/mol of  
catalyst/h, and the polymer possesses the following  
20 characteristics: Mn = 24 600. The chain incorporation  
of the monomer is isotactic (mm > 95%).

Example 3:

20 ml of distilled toluene are introduced,  
using a syringe, into a Schlenk tube (dried at 100°C  
25 for 2 h beforehand), connected to an argon line and  
equipped with a septum for introducing the reactants  
and with a magnetic stirrer. The toluene is degassed  
and then saturated with argon. Catalyst B (8 mg -  
0.01 mmol) is introduced and stirring is maintained  
30 until it has completely dissolved. Then 2 ml of  
1-pentene are introduced through the septum using a  
syringe. Polymerization is continued for 12 hours at  
ambient temperature with stirring. To neutralize the  
catalyst at the end of the reaction, 10 ml of methanol  
35 are injected. There is no precipitation of polymer.  
Following evaporation of the solvent, traces of  
unisolatable, low-mass oligomers are collected. The  
catalytic activity is very low and is estimated to be

less than 10 g of polymer/mol of catalyst/h.

Example 4:

20 ml of distilled toluene are introduced, using a syringe, into a Schlenk tube (dried at 100°C for 2 h beforehand), connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. The toluene is degassed and then saturated with argon. Precursor B (4 mg) is introduced and the solution is stirred at ambient temperature until its dissolution is complete. The catalytic solution is degassed three times, then a pressure of 1 bar of hydrogen is introduced. Hydrogenation is carried out at ambient temperature for 30 minutes. The solution turns from colorless to a vivid yellow. The hydrogen is subsequently driven off by a stream of argon (5 min). The reaction mixture is cooled to 0°C. Then 2 g of 1-pentene are introduced through the septum using a syringe. Polymerization is continued at 0°C for 18 hours. To neutralize the catalyst at the end of the reaction, 10 ml of methanol are injected. The precipitated polymer is then isolated by centrifuging, washed with 10 ml of methanol and dried under vacuum for 3 hours. 1.54 g of polymer are collected, corresponding to a conversion of 77% and an activity of 21 g of polymer/g of catalyst/h, said polymer possessing the following characteristics:  $M_n = 28\ 600$ . The chain incorporation of the monomer is isotactic ( $mm > 95\%$ ).

Example 5:

The procedure of example 4 is repeated, replacing the 1-pentene by 2 g of 1-hexene. The polymerization is continued at 0°C for 12 hours. 1.88 g of polymer are collected, corresponding to a conversion of 94% and an activity of 39.2 g of polymer/mol of catalyst/h, said polymer possessing the following characteristics:  $M_n = 53\ 000$ . The chain incorporation of the monomer is isotactic ( $mm > 95\%$ ).

Example 6:

The procedure of example 5 is repeated, conducting the polymerization at 20°C rather than at 0°C. 1.98 g of polymer are collected, corresponding to a conversion of 99% and an activity of 41 g of polymer/mol of catalyst/h, said polymer possessing the following characteristics:  $M_n = 12\,900$ . The chain incorporation of the monomer is isotactic ( $mm > 95\%$ ).

Example 7:

20 ml of distilled toluene are introduced, using a syringe, into a Schlenk tube (dried at 100°C for 2 h beforehand), connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. The toluene is degassed and then saturated with argon. Precursor B (40 mg) is introduced and the solution is stirred at ambient temperature until its dissolution is complete. The catalytic solution is degassed three times, then a pressure of 1 bar of hydrogen is introduced. Hydrogenation is carried out at ambient temperature for 30 minutes. The solution turns from colorless to a vivid yellow. The hydrogen is subsequently driven off by a stream of argon (5 min). Then 2 ml of 1-pentene are introduced through the septum using a syringe. Polymerization is continued at 20°C for 2 hours. Thereafter, 2 ml of methyl methacrylate are introduced with the septum. The solution changes in appearance to become opaque. The copolymerization is then continued for 2 hours. To neutralize the catalyst at the end of the reaction, 10 ml of methanol are injected. The precipitated polymer is then isolated by centrifuging and dried under vacuum for 3 hours. The polymer at this point has a sticky white appearance (presence of polyolefin characterized by a bimodal GPC possessing two maximum peaks of mass approximately 3 000 and 60 000). The mixture of polymers is subsequently washed with twice 10 ml of hexane (with stirring in hexane for 2 hours), which then allows the olefinic homopolymer to be removed with 10 ml of methanol. 0.21 g of polymer is



collected, corresponding to an activity of 5.2 g of polymer/g of catalyst, said polymer possessing the following characteristics: proportion of 1-pentene = 20% by weight, proportion of MMA = 80% by weight, Mn = 45 400. The poly(1-pentene) block is isotactic (mm > 95%).

Example 8:

The procedure of example 7 is repeated, replacing precursor B by 40 mg of precursor C, and replacing the 1-pentene by 2 ml of 1-hexene and the MMA by 2 ml of caprolactone. The polymer possesses the following characteristics: proportion of 1-hexene = 12% by weight, proportion of caprolactone = 88% by weight, Mn = 32 000. The poly(1-hexene) block is isotactic (mm > 95%).

Example 9:

Precursor B (100 mg) is introduced into a Schlenk tube (dried at 100°C for 2 h beforehand) connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. 3 ml of 1-hexene are introduced through the septum using a syringe, and the mixture is degassed three times and held under vacuum. A pressure of 1 bar of hydrogen is then introduced. The polymerization starts immediately, characterized by an exotherm. The reaction mixture becomes highly viscous and the reaction is continued at 20°C for 3 minutes. Thereafter, 2 ml of caprolactone are introduced via the septum. The polymerization is then continued for 1 hour. To neutralize the catalyst at the end of the reaction, 10 ml of methanol are injected. The precipitated polymer is then isolated by centrifuging, washed with methanol and dried under vacuum for 3 hours. The polymer is in the form of a dry, nontacky powder. 0.45 g of polymer is collected, corresponding to an activity of 4.5 g of polymer/g of catalyst, said polymer possessing the following characteristics: proportion of 1-hexene = 4.5% by weight, proportion of